

# Synthesis of chiral silver(I) diaminocarbene complexes from (*R,R*)-4,5-di-*tert*-butylimidazoline

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## Abstract

A preparation of chiral silver(I) diaminocarbene complexes was developed by treatment of imidazolinium salts derived from (*R,R*)-4,5-di-*tert*-butylimidazoline with silver(I) oxide. Complexes having the chirality on the heterocycle and methyl, benzyl or picolyl groups on the nitrogen atoms have been prepared. We also performed the synthesis of diaminocarbenes having in addition the chiral (*S*)-1-phenylethyl moiety on the nitrogen atoms. X-ray structures of two of these carbenes (*N,N'*-dimethyl and *N,N'*-dibenzyl) are presented. Several methods for the preparation of imidazolinium salts are described. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Imidazolinium salts; Silver(I); Diaminocarbenes; Chiral ligands; Crystal structures

## 1. Introduction

*N*-heterocyclic carbenes have recently emerged as an important family of ligands with electronic characteristics similar to those of the phosphines [1]. The use of imidazol-2-ylidene, thiazol-2-ylidene and imidazolidin-2-ylidene metal complexes rapidly showed an increased interest since it was demonstrated that they are efficient catalysts in important chemical transformations, such as Ni and Pd carbon–carbon coupling reactions, CO–ethylene copolymerisations, Ru-catalysed olefins metathesis and Rh catalysed hydrosilylations. Initially, the widespread use of catalysts with carbene ligands was limited due to their relatively difficult preparation. The first syntheses have utilised the free carbenes, obtained by deprotonation of the corresponding azolium salts, which are extremely air and moisture sensitive. Recent investigations have demonstrated that the free carbenes can be generated and directly trapped in situ [2]. Silver(I) carbene complexes derived from imidazolium salts were synthesised and characterised for the first time by Arduengo in 1993 [3]. These complexes

were obtained by reaction of the free carbene with silver triflate.

In our research to synthesise chiral imidazolidin-2-ylidene carbene complexes, we were particularly attracted by an alternative method described by Wang and Lin [4] in 1998. Indeed, these authors showed that a silver benzimidazol-2-ylidene complex could be easily obtained by treatment of the corresponding azolium salt with Ag<sub>2</sub>O. Moreover, this silver carbene complex acts as an effective carbene transfer agent for the synthesis of palladium or gold carbene complexes. This methodology was applied recently with success by McGuinness and Cavell [5] towards the synthesis of palladium imidazol-2-ylidene complexes which are efficient catalysts for C–C coupling reactions. Syntheses and structures of *N*-functionalised silver(I) carbene complexes derived from imidazolium salts were also reported by Danopoulos et al. in 2000 [6]. Such an approach is mild and compatible with the presence of acidic protons in chains of the azolium salts. Especially if applicable to the less acidic imidazolinium precursors, it could provide a very convenient method for the formation of chiral carbene complexes by overcoming many of the difficulties arising from the use of strong bases.

Synthesis of chiral diaminocarbene complexes remains an important challenge for organic chemists and

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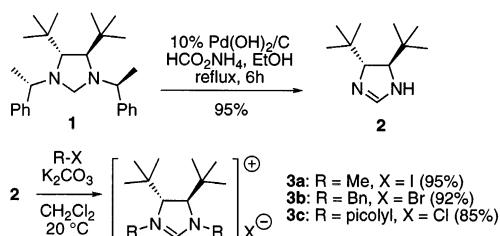
only a few catalysts have been reported [7]. We report here a versatile access to chiral imidazolin-2-ylidene silver(I) carbene complexes and X-ray structures of two of these compounds. The synthesis of the precursor imidazolinium salts from (*R,R*)-4,5-di-*tert*-butylimidazolidine is also reported.

## 2. Results and discussion

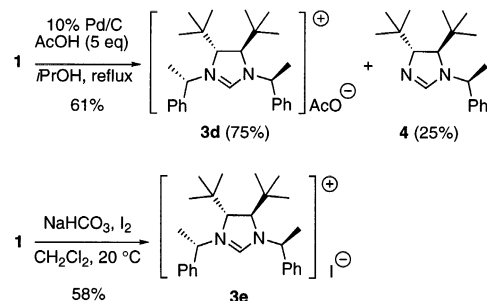
### 2.1. Synthesis of imidazolinium salts

We recently performed the synthesis of (*R,R*)-4,5-di-*tert*-butylimidazolidine (**2**) from the aминаl **1** [8] by a one step palladium-mediated hydrogenolysis and oxidation procedure [9]. This imidazoline **2** appeared to be an interesting precursor for the synthesis of imidazolinium salts (Scheme 1).

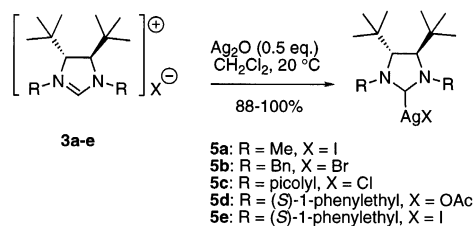
Indeed, **2** was easily alkylated in  $\text{CH}_2\text{Cl}_2$  at 20 °C using various halides. Precipitation with  $\text{Et}_2\text{O}$  and pentane and filtration led with 85–95% yields to the expected compounds **3a–c**. All these imidazolinium salts



Scheme 1. Preparation of imidazolinium salts from (*R,R*)-4,5-di-*tert*-butylimidazolidine (**2**).



Scheme 2. Preparation of imidazolinium salts by oxidation of aминаl **1**.



Scheme 3. Synthesis of Ag(I) carbene complexes.

showed the characteristic peak of the 2*H*-imidazolinium proton around 10–11 ppm (<sup>1</sup>H-NMR). However, we were also particularly attracted by the development of a methodology that allows us to oxidise the aминаl ring with preservation of the chiral moieties on the nitrogen atoms. In order to perform this reaction, we first tried the treatment of the imidazolidine **1** with 10% Pd/C in refluxing ethanol and no hydrogen donor. A slow reaction occurred, giving within 20 h the imidazoline **4** (90%) and a small amount (10%) of the expected salt **3d**. Addition of an excess of acetic acid gave the best results leading to a mixture of **3d** (75%) and **4** (25%). After neutralization, precipitation by addition of Et<sub>2</sub>O, filtration and drying under vacuum (0.5 mmHg) for 12 h at 100 °C to remove residual acetic acid, the expected salt **3d** was isolated in 61% yield. The characterization of the counterion in **3d** was quite difficult. We first considered that it may be an acetate ion since the elemental analysis of **3d** was in accordance with the calculated values of the monohydrate of the acetate salt (see Section 4). This hypothesis could be confirmed by the <sup>1</sup>H-NMR spectrum that showed (after drying) a signal at 2.12 ppm (3H) and no detectable acidic proton characteristic of a carboxylic acid. Nevertheless, the <sup>13</sup>C-NMR spectrum of **3d** exhibited signals which chemical shifts (20.9 and 177.2 ppm) were more consistent with the presence of one molecule of acetic acid than an acetate ion. For these reasons, the exact nature of the counterion (hydroxide or acetate) remains uncertain although this has no effect of the further reactions of the salt.

More recently, we found that a reported procedure using iodine and NaHCO<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> was also efficient to perform this oxidation [10] (Scheme 2). This reaction seemed quantitative since no aминаl **1** was detected in the crude by TLC. The imidazolinium salt **3e** has a very low solubility in most organic solvents and was isolated in 58% yield after dilution of the organic layer with Et<sub>2</sub>O, stirring with an aqueous solution of sodium bisulfite and filtration. <sup>1</sup>H-NMR spectroscopy (CDCl<sub>3</sub>) of this compound showed the characteristic peak of the 2*H*-imidazolinium proton at 10.21 ppm. Nevertheless, because of its low solubility and very high melting point (m.p. > 290 °C), we were unable to perform complementary analyses of **3e** [11].

### 2.2. Synthesis of silver(I) diaminocarbenes

Synthesis of silver(I) diaminocarbenes was very efficient using the Wang and Lin procedure. Treatment of the imidazolinium salts **3a–e** with 0.5 equivalents of silver oxide in CH<sub>2</sub>Cl<sub>2</sub> afforded quantitatively after few hours the expected carbenes **5a–e** (Scheme 3). This experiment was easily followed since Ag<sub>2</sub>O is insoluble in CH<sub>2</sub>Cl<sub>2</sub> and slowly disappeared in the course of the reaction.

These carbenes were fully characterised by  $^1\text{H}$ -NMR ( $\text{CDCl}_3$  or  $\text{DMSO}-d_6$ ).  $^1\text{H}$ -NMR spectra of all these compounds showed the complete disappearance of the  $2H$ -imidazolinium proton. The complexes **5a**, **5b** and **5d** gave only one signal for each group of equivalent protons. In **5c** and **5e**, two sets of similar peaks, characteristic of two compounds with a  $C_2$  symmetry, were observed. The ratio of these two similar forms was variable (from 2:1 to 9:1). The same phenomena was observed by Danopoulos et al. with some of their complexes [6] and the exact structure of these two forms could not be determined. However, we noticed that the NMR peaks of the minor form in **5c** and **5e**, had chemical shifts similar to those of the precursor salts but with no  $2H$ -imidazolinium proton signal detectable. Moreover, stirring a mixture of the two forms of **5c** in  $\text{CH}_2\text{Cl}_2$ , in the presence of  $\text{Ag}_2\text{O}$ , gave back to only one compound. From these observations, we deduced that the minor compound observed in some cases, may be the  $2D$ -imidazolinium salt obtained by deuteration of the carbene by the NMR solvent [12]. In compounds **5a–e**, the carbon between the two nitrogens atoms showed characteristic high chemical shifts of carbene signals in  $^{13}\text{C}$ -NMR (213.7 ppm for **5a**, 206 ppm for **5b**, 197.2 ppm for **5c**, 194.6 ppm for **5d**). Nevertheless, these chemical shifts are significantly higher than those described previously by Arduengo (183.6 ppm), Lin (188–189 ppm), Cavell (182 ppm) and Danopoulos on silver carbenes derived from imidazolium salts. No  $^{13}\text{C}-^{107,109}\text{Ag}$  coupling was observed in

the  $^{13}\text{C}$ -NMR studies of carbenes **5a–c** and **5e**. However, in **5d**, two doublets centered at 194.6 ppm were observed for the carbene signal. This multiplicity is probably due to the  $^{13}\text{C}-^{109}\text{Ag}/^{107}\text{Ag}$  couplings with coupling constants of 268 and 232 Hz. Two other signals corresponding to  $\text{Ph}-\text{CH}-\text{N}$  at 72.6/72.8 ppm and to  $\text{CH}_3-\text{CH}-\text{Ph}$  at 22.1/22.2 ppm, are also doubled. We could not determine if this phenomena was due to a  $^3J$  or  $^4J_{\text{C-Ag}}$  coupling or to a desymmetrisation of the molecule.

### 2.3. Structures of silver(I) diaminocarbenes

Structures of **5a** and **5b** were determined by X-ray spectroscopy. Figs. 1 and 3 show the ORTEP diagram of these two complexes. The crystallographic data for **5a** and **5b** are shown, respectively, in Tables 1 and 2. Selected bond lengths and angles are given in Table 3.

The structure of **5a** showed a dimer of a carbene–Ag–I unit, the two silver atoms being bridged by two iodides (Fig. 2). On the contrary, Lin and Arduengo have reported structures, for complexes derived from imidazolium or benzimidazolium salts, having two carbenes for one silver atom, this latter being associated with one molecule of  $\text{AgX}_2$ . Nevertheless, Lin already postulated in 1998 that an equilibrium should occur in solution between these two forms. More recently, Danopoulos et al. have reported that silver carbene complexes derived from imidazolium salts can adopt various structures in the solid state and also described

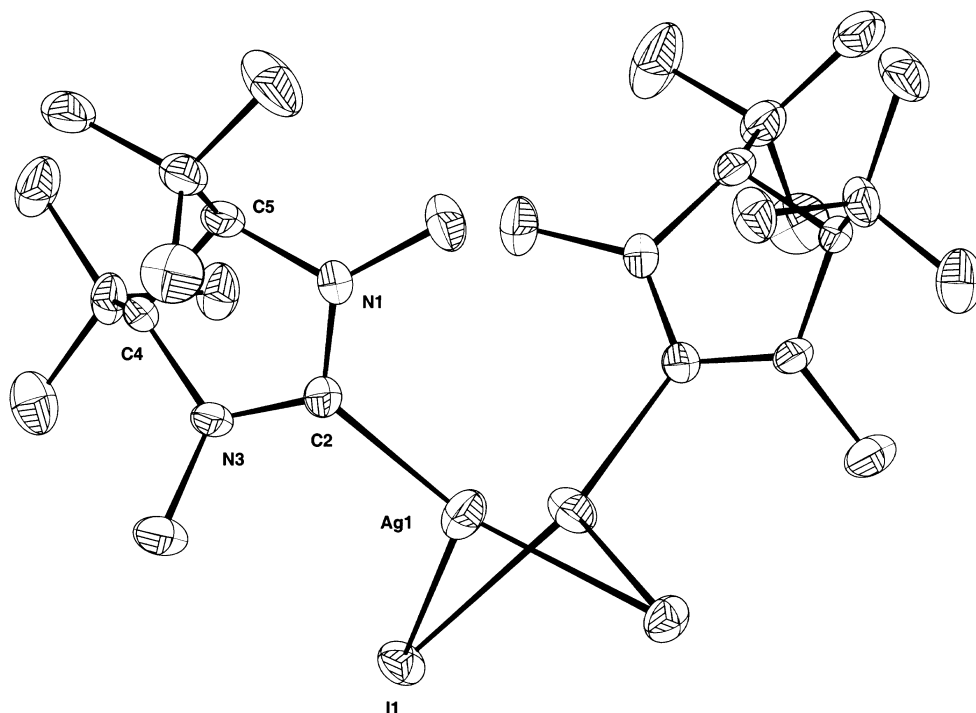


Fig. 1. ORTEP view of the dimeric structure of silver(I) diaminocarbene **5a**.

Table 1  
Crystallographic data for compound **5a**

|                                 |                                                                               |
|---------------------------------|-------------------------------------------------------------------------------|
| Compound                        | <b>5a</b>                                                                     |
| Formula                         | C <sub>26</sub> H <sub>52</sub> Ag <sub>2</sub> I <sub>2</sub> N <sub>4</sub> |
| Colour                          | Colourless                                                                    |
| Crystal class                   | Tetragonal                                                                    |
| Space group                     | P4 <sub>2</sub>                                                               |
| Z                               | 4                                                                             |
| Unit cell parameters            |                                                                               |
| <i>a</i> (Å)                    | 14.435 (3)                                                                    |
| <i>b</i> (Å)                    | 14.435 (3)                                                                    |
| <i>c</i> (Å)                    | 8.364 (2)                                                                     |
| <i>V</i>                        | 1742.8 (6)                                                                    |
| Radiation type                  | Mo Kα                                                                         |
| Wavelength (Å)                  | 0.71069                                                                       |
| Density                         | 1.70                                                                          |
| <i>M</i> (g mol <sup>−1</sup> ) | 890.28                                                                        |
| <i>μ</i> (cm <sup>−1</sup> )    | 29.14                                                                         |
| Temperature (K)                 | 295                                                                           |
| Size                            | 0.2 × 0.2 × 0.4                                                               |
| Shape                           | Stick                                                                         |
| Diffractometer                  | Enraf–Nonius Cad-4                                                            |
| Reflections measured            | 1793                                                                          |
| Independent reflections         | 1651                                                                          |
| <i>R</i> <sub>int</sub>         | 0.03                                                                          |

Table 2  
Crystallographic data for compound **5b**

|                                 |                                                    |
|---------------------------------|----------------------------------------------------|
| Compound                        | <b>5b</b>                                          |
| Formula                         | C <sub>25</sub> H <sub>34</sub> AgBrN <sub>2</sub> |
| Colour                          | Colourless                                         |
| Crystal class                   | Orthorhombic                                       |
| Space group                     | P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>      |
| Z                               | 4                                                  |
| Unit cell parameters            |                                                    |
| <i>a</i> (Å)                    | 9.603 (5)                                          |
| <i>b</i> (Å)                    | 15.778 (7)                                         |
| <i>c</i> (Å)                    | 16.607 (7)                                         |
| <i>V</i>                        | 2516 (2)                                           |
| Radiation type                  | Mo–K <sub>α</sub>                                  |
| Wavelength (Å)                  | 0.71069                                            |
| Density                         | 1.45                                               |
| <i>M</i> (g mol <sup>−1</sup> ) | 550.33                                             |
| <i>μ</i> (cm <sup>−1</sup> )    | 24                                                 |
| Temperature (K)                 | 295                                                |
| Size                            | 0.2 × 0.3 × 0.3                                    |
| Shape                           | Parallelepiped                                     |
| Diffractometer                  | Enraf–Nonius Cad-4                                 |
| Reflections measured            | 2540                                               |
| Independent reflections         | 2515                                               |

carbenes complexes having structures similar to **5a**, with a weak Ag–Ag interaction. The Ag–C(1) bond distance in **5a** (2.12 Å) is comparable but a bit longer than the one found by Lin (2.073 and 2.052 Å) and Danopoulos (2.06–2.1 Å). The Ag(1)–I(1)–Ag(1')–I(1') structure is not planar and the Ag–Ag distance of 3.02 Å can be attributed to a weak interaction between

the two metals. The structure of **5b** showed the same carbene–Ag–X unit but this complex crystallised as a monomer.

Table 3  
Selected bond lengths (Å) and bond angles (°) for **5a** and **5b**

|                     | <b>5a</b>  | <b>5b</b> |
|---------------------|------------|-----------|
| <i>Bond lengths</i> |            |           |
| Ag(1)–C(2)          | 2.120(8)   | 2.089(17) |
| N(1)–C(2)           | 1.324(13)  | 1.28(2)   |
| N(3)–C(2)           | 1.31(1)    | 1.32(2)   |
| Ag(1)–Ag(1')        | 3.0196(14) | –         |
| Ag(1)–I(1)          | 2.6251(8)  | –         |
| Ag(1)–Br(1)         | –          | 2.401(3)  |
| <i>Bond angles</i>  |            |           |
| N(1)–C(2)–N(3)      | 108.8(7)   | 109.5(15) |
| Ag(1)–C(2)–N(1)     | 123.2(6)   | 123.2(12) |
| Ag(1)–C(2)–N(3)     | 127.4(6)   | 126.9(13) |
| I(1)–Ag(1)–C(2)     | 166.3(2)   | –         |
| Br(1)–Ag(1)–C(2)    | –          | 175.2(5)  |
| C(2)–N(3)–C(4)      | 113.5(6)   | 114.5(15) |
| C(2)–N(1)–C(5)      | 112.8(6)   | 113.7(14) |

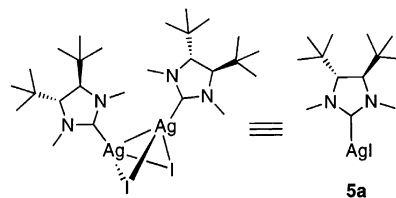


Fig. 2. Dimeric and monomeric structures of **5a**.

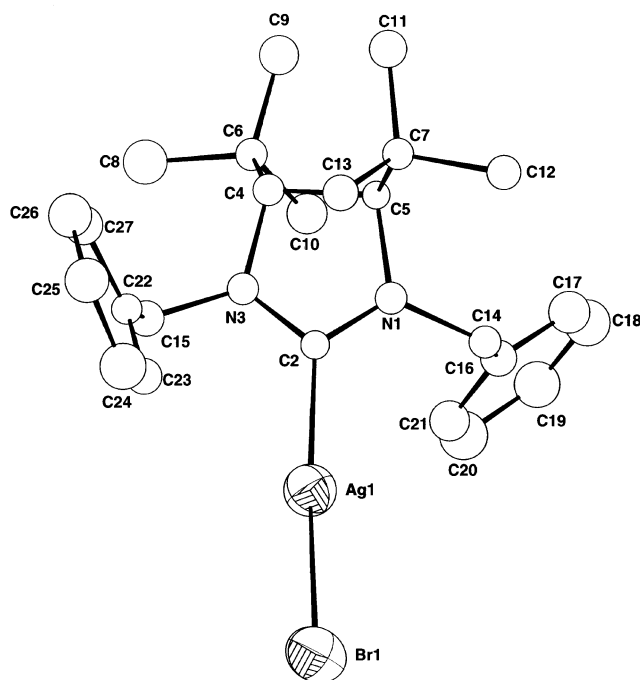


Fig. 3. ORTEP view of silver(I) diaminocarbene **5b**.

### 3. Conclusion

This work provides a convenient method for the synthesis of various chiral Ag(I) carbene complexes from imidazolinium salts. X-ray structures of **5a** and **5b** clearly show a monomeric carbene–Ag–X unit. Further utilisation of these compounds for the preparation of transition metal carbene complexes and their use in catalytic reactions is under investigation.

### 4. Experimental

All experiments were carried out under argon. Silver(I) oxide 99 + % was purchased from Acros. Solvents were of analytical grade type and used without special drying or distillation. NMR spectra were recorded on a Bruker ARX 400 or AC 200 Q instrument, in CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub> as the solvent. Optical rotations were measured on a Perkin–Elmer 343.

#### 4.1. Synthesis of imidazoline (**2**)

To a solution of imidazolidine **1** [8] (1 mmol) in EtOH (20 ml), were added Pd(OH)<sub>2</sub>/C (0.1 mmol) and ammonium formate (10 mmol). The mixture was refluxed for 6 h, filtered and concentrated. To the residue were added Et<sub>2</sub>O (15 ml) and K<sub>2</sub>CO<sub>3</sub> (0.5 g) and the suspension was stirred for 1 h, filtered and concentrated to give the imidazoline **2** as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.86 (s, 18H), 3.27 (s, 2H), 4.8 (s, 1H), 7.05 (s, 1H). <sup>13</sup>C NMR: δ 24.5, 33.2, 69.1, 150.7.

#### 4.2. Typical procedure for the synthesis of imidazolinium salts (**3a–c**)

To a solution of imidazoline **2** (1 mmol.) in CH<sub>2</sub>Cl<sub>2</sub> (5 ml) were added K<sub>2</sub>CO<sub>3</sub> (0.5 g) and the halide (2.1 mmol.). The solution was stirred for 12 h at 20 °C, filtered through Celite and concentrated. The residue was taken off in Et<sub>2</sub>O or pentane (15 ml). The white precipitate formed was filtered, washed several times with pentane and dried under vacuum to afford the expected salts (85–95%) as white solids.

##### 4.2.1. (4*R*,5*R*)-1,3-Dimethyl-4,5-di-*tert*-butylimidazolinium iodide (**3a**)

M.p. 270–271 °C. [ $\alpha$ ]<sub>D</sub><sup>20</sup> = –54.4 (*c* 2.02, CHCl<sub>3</sub>). Anal. Calc. for C<sub>13</sub>H<sub>27</sub>IN<sub>2</sub> (*M*<sub>w</sub> = 338.27): C, 46.16; H, 8.05; N, 8.28. Found: C, 45.47; H, 8.36; N, 7.98. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 1.02 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 3.38 (s, 2H, CH–N), 3.45 (s, 6H, CH<sub>3</sub>–N), 10.07 (s, 1H, N–CH=N<sup>+</sup>). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ 27.5, 37.2, 38.7, 75.5, 160.6.

##### 4.2.2. (4*R*,5*R*)-1,3-Dibenzyl-4,5-di-*tert*-butylimidazolinium bromide (**3b**)

M.p. 249–250 °C. [ $\alpha$ ]<sub>D</sub><sup>20</sup> = –114.3 (*c* 1.6, CHCl<sub>3</sub>). Anal. Calc. for C<sub>25</sub>H<sub>35</sub>BrN<sub>2</sub> (*M*<sub>w</sub> = 443.46): C, 67.71; H, 7.96; N, 6.32. Found: C, 66.55; H, 7.79; N, 6.15. <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>): δ 0.68 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 3.38 (s, 2H, CH–N), 4.47 (d, 2H, *J* 14 Hz, Ph–C(H')H–N), 5.53 (d, 2H, *J* 14 Hz, Ph–C(H)H'–N), 7.38–7.43 (m, 6H, *Ph*), 7.54–7.56 (m, 4H, *Ph*), 11.12 (s, 1H, N–CH=N<sup>+</sup>). <sup>13</sup>C-NMR δ 26.5, 35.8, 53.5, 69.7, 129.4, 130, 132.9, 159.6.

##### 4.2.3. (4*R*,5*R*)-1,3-Dipicolyl-4,5-di-*tert*-butylimidazolinium chloride (**3c**)

M.p. 148–149 °C. [ $\alpha$ ]<sub>D</sub><sup>20</sup> = –52 (*c* 1, CH<sub>2</sub>Cl<sub>2</sub>). Anal. Calc. for C<sub>23</sub>H<sub>33</sub>ClN<sub>4</sub> (*MW* = 400.99): C, 68.89; H, 8.30; N, 13.97. Found: C, 66.42; H, 8.56; N, 13.44. <sup>1</sup>H-NMR (200 MHz, DMSO-*d*<sub>6</sub>): δ 0.72 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 3.82 (s, 2H, CH–N), 4.67 (d, 2H, *J* 14.5 Hz, Ar–C(H')H–N), 5.45 (d, 2H, *J* 14.5 Hz, Ar–C(H)H'–N), 7.23–7.33 (m, 2H, *Ar*), 7.69–7.87 (m, 4H, *Ar*), 8.55 (d, 2H, *J* 5 Hz, *Ar*), 10.71 (s, 1H, N–CH=N<sup>+</sup>). <sup>13</sup>C-NMR (DMSO-*D*<sub>6</sub>): δ 26.1, 36.3, 54, 71.5, 124.5, 124.7, 138.4, 150.3, 154.4, 160.5.

##### 4.2.4. (4*R*,5*R*)-1,3-[(*S*)-1-phenylethyl]-4,5-di-*tert*-butylimidazolinium acetate (**3d**)

A mixture of aminoral **1** (1 mmol), acetic acid (4 mmol) and Pd/C (0.1 mmol.) in *i*PrOH (20 ml) was refluxed for 20 h, filtered through Celite and concentrated. The residue was taken off in CH<sub>2</sub>Cl<sub>2</sub> (15 ml) and solid K<sub>2</sub>CO<sub>3</sub> was added. The suspension was stirred for 0.5 h, filtered and concentrated. The residue was taken off in Et<sub>2</sub>O (15 ml). The white precipitate formed was filtered, washed several times with pentane and dried under vacuum (0.1 mmHg) at 100 °C to give 275 mg (61%) of **3d**. Recrystallisation in ethylacetate and a small amount of CHCl<sub>3</sub> led to small, thin, colourless needles.

[ $\alpha$ ]<sub>D</sub><sup>20</sup> = –163 (*c* 1.77, CHCl<sub>3</sub>). Anal. Calc. for C<sub>29</sub>H<sub>42</sub>N<sub>2</sub>O<sub>2</sub> (*M*<sub>w</sub> = 450.66): C, 77.29; H, 9.39; N, 6.22. Calc. for C<sub>29</sub>H<sub>42</sub>N<sub>2</sub>O<sub>2</sub>·H<sub>2</sub>O: C, 74.32; H, 9.46; N, 5.98. Found: C, 74.02; H, 9.12; N, 6.06. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 0.59 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 2.12 (s, 3H, CH<sub>3</sub>CO<sub>2</sub><sup>–</sup>), 2.20 (d, 6H, *J* 7.4 Hz, CH<sub>3</sub>–CH), 3.29 (s, 2H, *t*Bu–CH–N), 4.61 (q, 2H, *J* 7.4 Hz, CH–CH<sub>3</sub>), 7.30–7.71 (m, 10H, *Ph*), 11.25 (s, 1H, N–CH=N<sup>+</sup>). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 20.9, 24.3, 27.1, 36.4, 62.3, 71.9, 128.6, 130.1, 130.4, 139.8, 157.5, 177.2.

##### 4.2.5. (4*R*,5*R*)-1,3-[(*S*)-1-phenylethyl]-4,5-di-*tert*-butylimidazolinium iodide (**3e**)

To a mixture of aminoral **1** (1 mmol.) and NaHCO<sub>3</sub> (1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 ml) was added dropwise a solution of iodine (1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 ml). The mixture was stirred 24 h at 20 °C. Et<sub>2</sub>O (50 ml) and sodium bisulfite

(aqueous solution) was added. The suspension was stirred until decoloration and appearance of a white precipitate in the organic phase. The solution was filtered and the precipitate was washed with Et<sub>2</sub>O and dried to afford 290 mg (58%) of the expected compound as a white solid.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 0.60 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 2.28 (d, 6H, *J* 7.4 Hz, CH<sub>3</sub>–CH), 3.35 (s, 2H, 'Bu–CH–N), 4.64 (q, 2H, *J* 7.4 Hz, CH–CH<sub>3</sub>), 7.25–7.77 (m, 10H, *Ph*), 10.21 (s, 1H, N–CH=N<sup>+</sup>).

### 4.3. Typical procedure for the synthesis of **5a–e**

To a solution of imidazolium salt **3a–e** (1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 ml) was added Ag<sub>2</sub>O (0.5 mmol). The mixture was stirred at 20 °C until complete consumption of the precipitate (4–20 h), filtered through Celite and concentrated to give quantitatively the expected compounds as crystalline solids.

#### 4.3.1. (4*R*,5*R*)-1,3-Dimethyl-4,5-di-*tert*-butylimidazolin-2-ylidene silver(I) iodide (**5a**)

[α]<sub>D</sub><sup>20</sup> = –93 (*c* 1, CHCl<sub>3</sub>). Anal. Calc. for C<sub>13</sub>H<sub>26</sub>AgIn<sub>2</sub> (*M*<sub>w</sub> = 445.1): C, 35.08; H, 5.89; N, 6.29. Found: C, 36.89; H, 6.60; N, 6.37%. <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 0.87 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 3.21 (s, 6H, CH<sub>3</sub>–N), 3.34 (s, 2H, CH–N). <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>) δ 32.9, 41.7, 45.8, 80.5, 213.7 (N–C–N). The single crystals of **5a** suitable for X-ray diffraction analysis were obtained by recrystallisation from CH<sub>2</sub>Cl<sub>2</sub>, Et<sub>2</sub>O and pentane mixture.

#### 4.3.2. (4*R*,5*R*)-1,3-Dibenzyl-4,5-di-*tert*-butylimidazolin-2-ylidene silver(I) bromide (**5b**)

[α]<sub>D</sub><sup>20</sup> = –57 (*c* 0.68, CH<sub>2</sub>Cl<sub>2</sub>). Anal. Calc. for C<sub>25</sub>H<sub>34</sub>AgBrN<sub>2</sub> (*M*<sub>w</sub> = 550.3): C, 54.56; H, 6.23; N, 5.09. Found: C, 55.24; H, 6.42; N, 4.89%. <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>) δ 0.68 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 3.24 (s, 2H, CH–N), 4.50 (d, 2H, *J* 14.5 Hz, Ph–C(H')H–N), 5.12 (d, 2H, *J* 14.5 Hz, Ph–C(H)H'–N) 7.3–7.42 (m, 10H, *Ph*). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ 27.3, 35.7, 56.5, 71.2, 128.8, 129.2, 129.7, 135.4, 206 (N–C–N).

The single crystals of **5b** suitable for X-ray diffraction analysis were obtained by recrystallisation from CH<sub>2</sub>Cl<sub>2</sub> and hexane mixture.

#### 4.3.3. (4*R*,5*R*)-1,3-Dipicolyl-4,5-di-*tert*-butylimidazolin-2-ylidene silver(I) chloride (**5c**)

[α]<sub>D</sub><sup>20</sup> = –17 (*c* 0.9, CH<sub>2</sub>Cl<sub>2</sub>). Anal. Calc. for C<sub>23</sub>H<sub>32</sub>AgClN<sub>4</sub> (*M*<sub>w</sub> = 507.8): C, 54.40; H, 6.35; N, 11.03. Found: C, 55.39; H, 6.71; N, 11.09%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 0.67 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 3.54 (s, 2H), 4.65 (d, 2H, *J* 14.5 Hz, N–CH–Ar), 5.03 (d, 2H, *J* 14.5 Hz, N–CH'–Ar), 7.14–8.55 (m, 8H, *Ar*). <sup>13</sup>C-NMR δ 27.6, 36.4, 58.6, 72.8, 124.2, 124.8, 138.12, 150.4, 156.9, 197.2 (N–C–N).

#### 4.3.4. (4*R*,5*R*)-1,3-bis-[(*S*)-1-Phenylethyl]-4,5-di-*tert*-butylimidazolin-2-ylidene silver(I) acetate (**5d**)

[α]<sub>D</sub><sup>20</sup> = –71 (*c* 0.5, CH<sub>2</sub>Cl<sub>2</sub>). Anal. Calc. for C<sub>29</sub>H<sub>41</sub>AgN<sub>2</sub>O<sub>2</sub> (*M*<sub>w</sub> = 557.5): C, 62.48; H, 7.41; N, 5.02. Found: C, 61.35; H, 7.88; N, 4.94%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 0.60 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 2.17 (d, 6H, *J* 7 Hz, CH<sub>3</sub>–CH), 2.18 (s, 3H, CH<sub>3</sub>CO<sub>2</sub>Ag), 3.15 (s, 2H, 'Bu–CH–N), 4.65 (q, 2H, *J* 7 Hz, CH–CH<sub>3</sub>), 7.22–7.61 (m, 10H, *Ph*). <sup>13</sup>C-NMR δ 22.1, 22.2 (CH<sub>3</sub>–CH–Ph), 23.2, 26.6, 35.1, 59.6 ('Bu–CH–N), 72.6, 72.9 (Ph–CH–N), 127.9, 128.2, 128.7, 140.8, 178.7, 194.6 (d + d, *J* 232 and 268 Hz, N–C–N).

#### 4.3.5. (4*R*,5*R*)-1,3-bis-[(*S*)-1-Phenylethyl]-4,5-di-*tert*-butylimidazolin-2-ylidene silver(I) iodide (**5e**)

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 0.61 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 2.15 (d, 6H, *J* 7.4 Hz, CH<sub>3</sub>–CH–N), 2.02 (s, 2H, 'Bu–CH–N), 4.66 (q, 2H, *J* 7.4 Hz, CH<sub>3</sub>–CH–N), 7.23–7.72 (m, 10H). <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>) δ 22.1, 26, 34.9, 58.2, 72.1, 127.9, 128.4, 141.3. The carbene carbon was not observed.

## 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 160043 for compound **5a** and 160044 for **5b**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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